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Alternative Fiber Sources from *Gracilaria Sp* and *Eucheuma Cottonii* for Papermaking

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Abstract - Private sectors have invested in the technology to grow some Gelidialian red algae families and also tried to convert the algae to pulp and paper over the last few years in order to replace raw materials from wood. Several modern systems with their all complexities which are similar to the wood pulp-based papermaking technology have been offered to overcome any recent issues settle in the converting process. Chemical bleaching agents have even been still a standard treatment that must be established for properly converting the algae pulp to a sheet of paper. In this present work, the two genus of red algae, called *Gracilaria* and *Eucheuma*, were simply processed to make pulps without use of any bleaching chemical agents. The potential use of pulps made of the red algae as raw materials for papermaking was mechanically studied by testing the sheets made of the red algae through a tensile test at a room temperature under 20 mm/min according to ASTM D 828-97 (2002). Tensile properties of the proposed algae-based paper sheets obtained under the constant rate are discussed. Tensile properties of the selected wood-based paper sheets obtained under the same condition are also presented in this paper. The results showed that pulps made of the red algae would be the alternative to those of the wood and other natural fibers as raw materials for papermaking.

Key words - red algae, papermaking, paper sheet, tensile properties

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Introduction

In the early history of paper, paper was made from bamboo, hemp, fishnets, barks and flax rags [1-4] and never includes a discussion of wood pulp. The years after the industrial revolution saw the invention of faster printing machines with technological advancements, demand for paper increases. This caused paper makers to turn to a source of pulp that was plentiful and relatively easy to process. Wood then soon became the most popular source of pulp for paper. In fact, it is now the source of approximately 95% of the world's paper [5]. In a few coming years up to 2020, the global production of pulp and paper is expected to increase by 77% due to the increasing world population, in addition to improve literacy and quality of life worldwide [6]. The continued high growth in paper consumption will hence lead to increase the demand for fiber, creating additional pressure on the world's diminishing forest resources. To maintain paper industry growth, development of non-wood fibers or alternative fibers has been one of creative strategies and plans to ensure a sustainable fiber supply including reforestation programs, plantation management and recycling [1, 3-6].

Natural fibers, generally plant-based fibers like corn, wheat straw, sugar cane, sisal, banana, and kenaf have been more frequently utilized and studied so far and a large number of literatures have been reported on pulp and paper based on these plant-based natural fibers [7-16]. In recent years, with emphasis of growing environmental awareness, such natural fibers have been increasingly used as alternative non-wood fibers for papermaking. Sustainability of supply of such plant-based fibers for papermaking, however, will further face the same problem with the land in the earth that gradually reduces due to world population and consumption in the future. Finally, scientists have discovered an alternative raw material for paper that is of the red algae (*Gelidium amansii* and *Gelidium corneum*) [17]. Fiber collected from the red algae has been believed as an alternative fiber for papermaking [17]. In utilizing red algae fiber as a reinforcing material in composite systems, Lee et al. [18] reported that the bleached red algae fiber showed the higher thermal stability than that of the crystalline cellulose. As reported by Sim et al. [19], characterization of red algae fiber showed that the length and diameter of fiber are ten times smaller than plant-based natural fibers. It was also then revealed that utilizing the red algae fiber as a reinforcing material was effective for obtaining the uniform properties of biocomposites since the shape of the red algae fiber was much uniform.

Firstly were recognized in Bali, Indonesia, two red algae species, *Gelidium amansii* and *Gelidium corneum*, are currently being developed intensively by private sectors in Lombok, Indonesia. Both red algae usually grow at around 3-10 % per day (dry weight) in natural environment during the growing season [17] can even rapidly grow up to 20 % per day in cultivation. Not like wood that requires ten of years to grow. Indeed, the red algae cultivation can be done by anyone since it is easily developed. With the easy cultivation and the incredible area of the sea of Indonesia, development of alternative fiber from red algae, hence, not only can ensure a sustainable fiber supply for papermaking but also is far from conflict with environmental interests.

In this work, two edible seaweeds of the red algae species, *Gracilaria sp* and *Eucheuma cottonii* [20], which are, respectively, from the genus of *Gracilaria* and *Eucheuma* cultivated in Indonesia waters [21], are selected to mechanically study the potential use of the red algae pulps as raw material for papermaking.

Materials and Methods

Pulp and Paper Preparation Method

Two red algae, *Gracilaria sp* and *Eucheuma cottonii*, as shown in Figure 1, were respectively collected from the East Coastal and the West Coastal of Province of Aceh, Indonesia. Before soaking them into water for 24h, the red algae were separately washed. The soaked algae were chipped then into a size of approximately 2 cm. Boiling the algae were then separately performed up to 120°C by setting the water to the algae chip ratio at 10. This latter temperature was slowly further switched down and finally maintained at 80°C for 1 hour. Chemical bleaching agents which have been a standard treatment that must be established for properly converting the algae pulp to a sheet of paper was not used. Filtration was then separately conducted to collect a small amount of solid materials. The final filtration was repeatedly conducted after re-boiling the solid materials with the same method. The solid materials which were obtained from the final filtration of each of the algae were then prepared to make pulp as raw material for papermaking. This latter solid materials are mostly consists of endofibers. Pulp of each of the algae was made by mixing their endofibers separately with glycerin as plasticizer and natural adhesive made of tapioca using a stationary blender consists of a blender jar with double blade at the bottom rotated by a motor. The mixture was separately then poured over a frame which had nylon screen stapled to it at different designed thickness. A mixture without tapioca was also prepared for a reference paper sheet. The handmade sheet of paper was further obtained after sun-dried for 8 hours. This latter sheet was then hot-pressed using flatiron. Density of the sheets was then measured manually after measuring the final thickness and weight of the sheets. Thickness of the hot-pressed sheets was measured using a portable digital thickness micrometer (Mitutoyo, Japan) while weight of the hot-pressed sheets was measured using digital laboratory balance (Sartorius P6, Germany).

SEM/EDS Method

SEM/EDS method is a micro-chemical analysis using scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS). This SEM/EDS analysis was performed using Tabletop Microscope (TM3000, Hitachi, Japan) to analyze non-destructively the associated elemental in the microstructure of the algae shape and to distinguish the morphology of the red algae fiber by capturing the cross sectional shape images of the red algae.

Tensile Test Method

A tensile test under a constant rate of 20 mm/min was performed at room temperature to measure the tensile properties of the red algae paper such as elongation, tensile ultimate load, ultimate tensile strength and tensile energy absorption. Testing of both handmade recycled paper and office copy paper (A4, 70 gsm) sheets was also conducted to provide the representative tensile properties of wood-based papers. The sheets of the paper was further prepared into strips to meet tensile test specimen requirements according to ASTM D 828-97 (2002). ASTM D 828-97 (2002) is a standard test method for tensile properties of paper and paperboard using constant rate of elongation. Geometry and dimension of the tensile test specimen of the algae paper are illustrated in Figure 2.

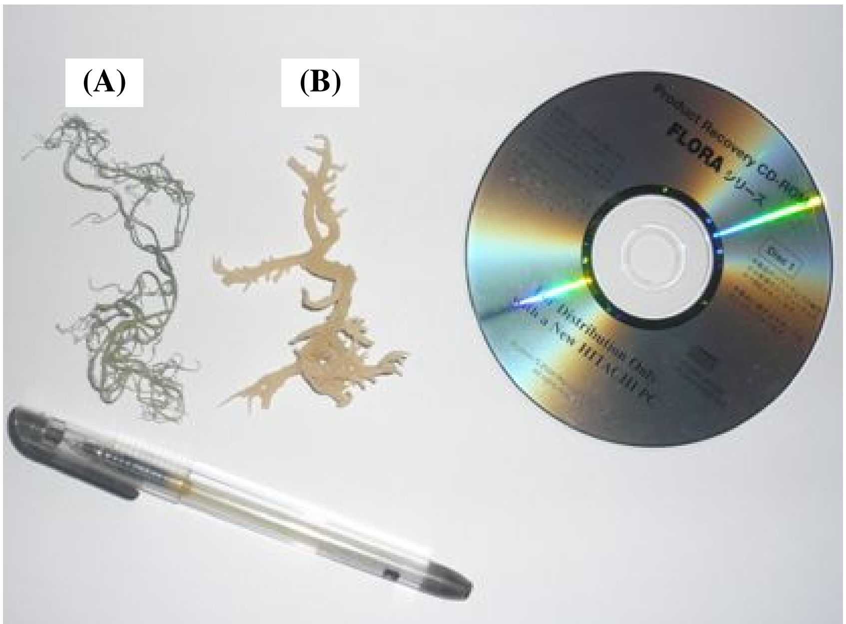

Figure 1. Red algae species (dried), *Gracilaria sp* (A) and *Eucheuma cottonii* (B)

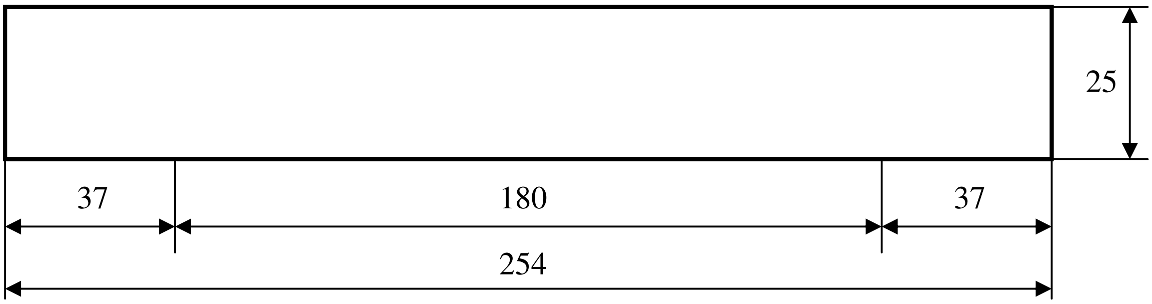

Figure 2. Geometry and dimension of the tensile test specimen (Unit in mm)

Results and Discussion

SEM/EDS Results

SEM image of the cross sectional shape of dried *Gracilaria sp* and *Eucheuma cottonii* is shown in Figure 3 and Figure 5, respectively. Meanwhile, Figure 4 and Figure 6, respectively, show the magnification images of their cross sectional shape. With these latter magnification images, morphology of the red algae fibers can be clearly distinguished. Fibers of the *Eucheuma cottonii*, which are ribbon-like, are more uniform than those of the *Gracilaria sp*.

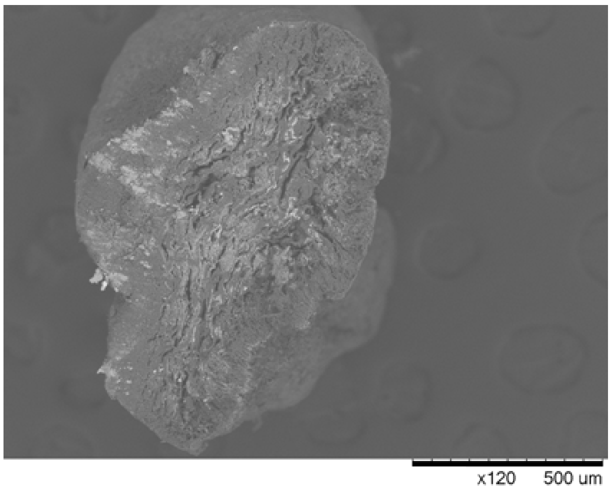

Figure 3. SEM image of cross sectional shape of dried *Gracilaria sp*

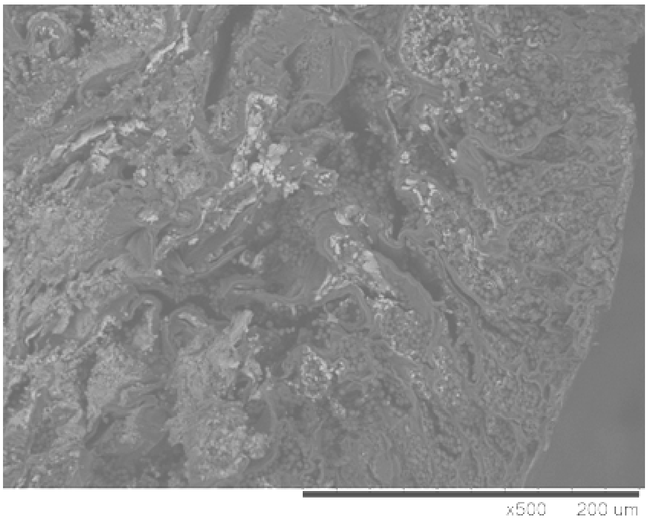

Figure 4. SEM image of magnification of the cross sectional of dried *Gracilaria sp*

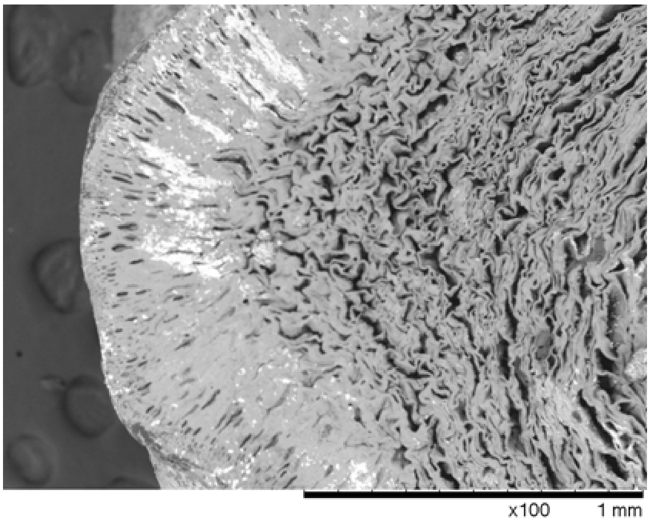

Figure 5. SEM image of cross sectional shape of dried *Eucheuma cottonii*

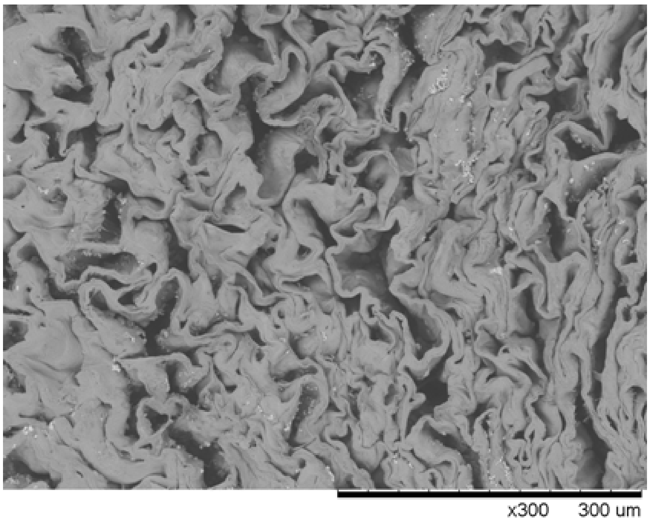

Figure 6. SEM image of magnification of the cross-section of dried *Eucheuma cottonii*

Chemical results of the elemental mapping of the algae microstructure by SEM/EDS are shown in Table 1. Except carbon (C), sodium (Na) and sulfur (S), Table 1 generally also shows that composition of elements in both *Gracilaria sp* and *Eucheuma cottonii* does not significantly show a difference. The results showed that carbon (C) and oxygen (O) were the most important elements in both *Gracilaria sp* and *Eucheuma cottonii*. *Gracilaria sp* consisted of carbon of about 52% higher than that of *Eucheuma cottonii*. Meanwhile, composition of sodium dan sulfur in *Eucheuma cottonii* was about 92% and 183%, respectively, higher than those of in *Gracilaria sp*.

Table 1. Chemical composition of algae microstructure by SEM/EDS

Algae Species	Elements (%)					
	C	O	Na	S	Cl	K
Gracilaria sp.	32.35	44.91	1.70	3.58	6.50	10.61
Eucheuma Cottonii	21.27	49.02	3.26	10.15	7.03	9.28

Handmade Sheets of Red Algae Paper

The handmade sheets of the red algae paper are shown in Figure 7. The linear shrinkage through the thickness was significantly exhibited by any sheets made of the both red algae. It was then measured and is plotted in Figure 8. This latter figure shows that the sheets made of *Eucheuma cottonii* exhibited the higher shrinkages than those of *Gracilaria* sp. Finally, after hot-pressing using flatiron, it was identified that for the thickness was about 0.25 mm and 0.41 mm, density of the sheet made of *Gracilaria sp* was 0.18 g/cm^3 and 0.25 g/cm^3, respectively, while for the thickness was about 0.15 mm and 0.26 mm, density of the sheet made of *Eucheuma cottonii* was 0.33 g/cm^3 and 0.55 g/cm^3, respectively.

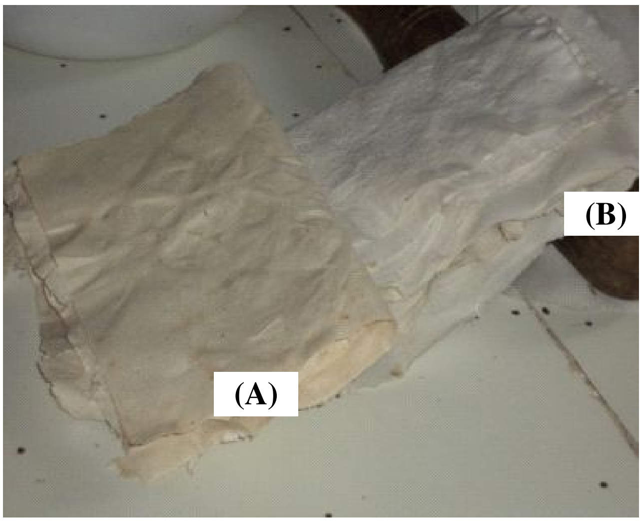

Figure 7. Handmade sheets of paper from *Gracilaria sp* (A) and *Eucheuma Cottonii* (B)

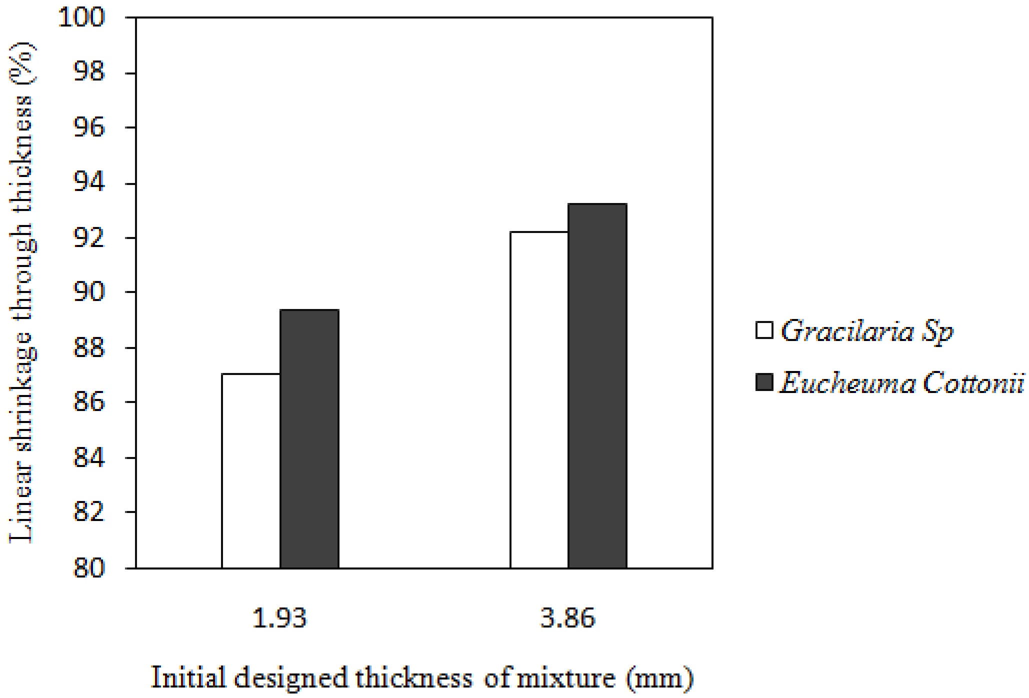

Figure 8. Linear shrinkages through thickness of paper sheets made of both red algae

Tensile Test Results

Tensile test results such as elongation, tensile ultimate load, ultimate tensile strength and tensile energy absorption are respectively presented in Figures 9, 10, 11, 12, 13, 14, 15 and 16. Except, the tensile strength of sheets made of the office copy paper (A4, 70 gsm), the other tensile properties of handmade of both recycled paper and office copy paper sheets are presented in the figures to show the representative tensile properties of wood-based papers. The tensile strength of the sheets made of the office copy paper A4 are separately presented in Table 2. Figures 9 and 10 show that ductility of the sheets made of *Eucheuma cottonii* is generally better than the other sheets. The lower ductility of paper made of *Gracilaria sp* might be influenced by the higher composition of carbon (see Table 1). Although the role of carbon in the paper materials is still yet unknown at the present study, in many cases of materials, especially steel materials, for example, high composition of carbon leads to low ductility of the steels. The values of the ultimate load between the sheets made of *Gracilaria sp* and made of *Eucheuma cottonii* as shown in Figure 11 and Figure 12 are almost comparable.

The comparable value of the ultimate load, however, cannot ensure the tensile strength of sheets made of the both red algae is comparable (see Figures 13 and 14). The tensile strength of the sheets made of *Gracilaria sp* is mostly influenced by the thickness of their sheets. Due to their lower shrinkages, the sheets made of *Gracilaria sp* were thicker than those of *Eucheuma cottonii* which then finally promoted the enlargement of their cross-section area. Nevertheless, ductility of the sheets made of *Gracilaria sp* was rather better than that of both the recycled and office copy paper sheets. Tapioca as an adhesive contributed to the improvement of their tensile properties since blending it into the mixture significantly improved their tensile properties. Figures 10, 14 and 16 show that the tensile properties of the sheets made of *Gracilaria sp* such as tensile elongation, ultimate strength and absorbed energy are even better than those of both the recycled and office copy paper sheets with use of the tapioca. These results show that pulps of the red algae are potential as raw materials for papermaking.

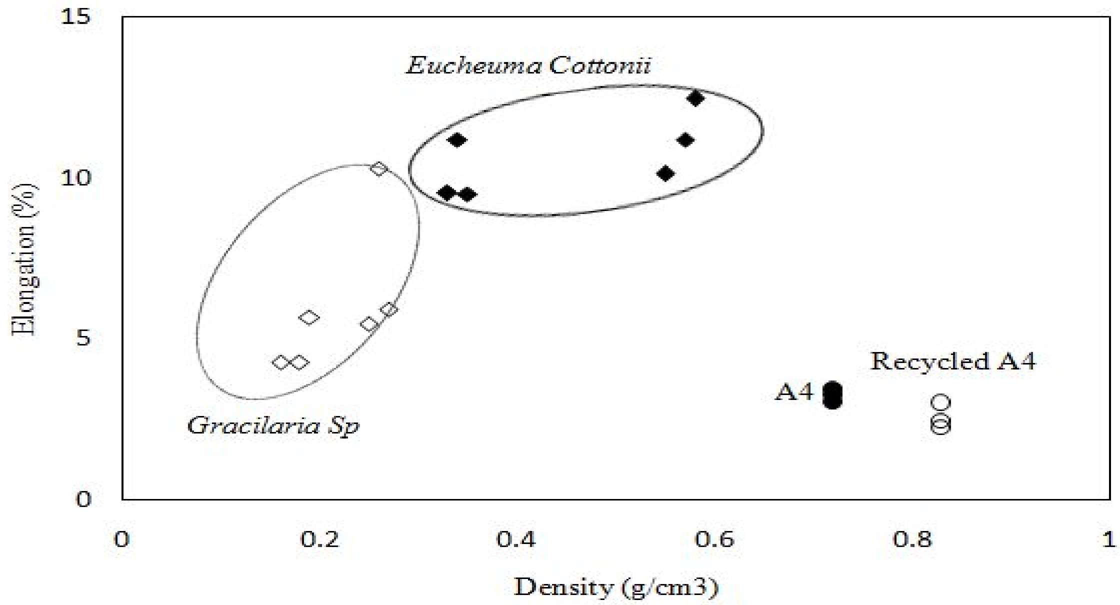

Figure 9. Density-based elongation of algae paper without use of adhesive

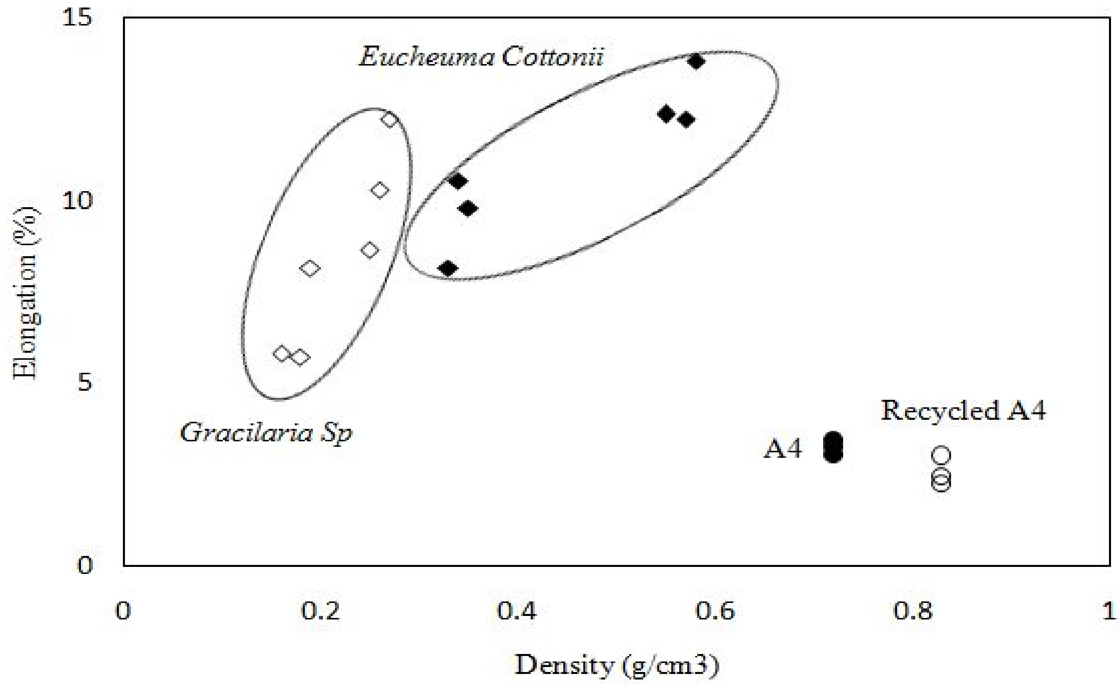

Figure 10. Density-based elongation of algae paper with use of adhesive

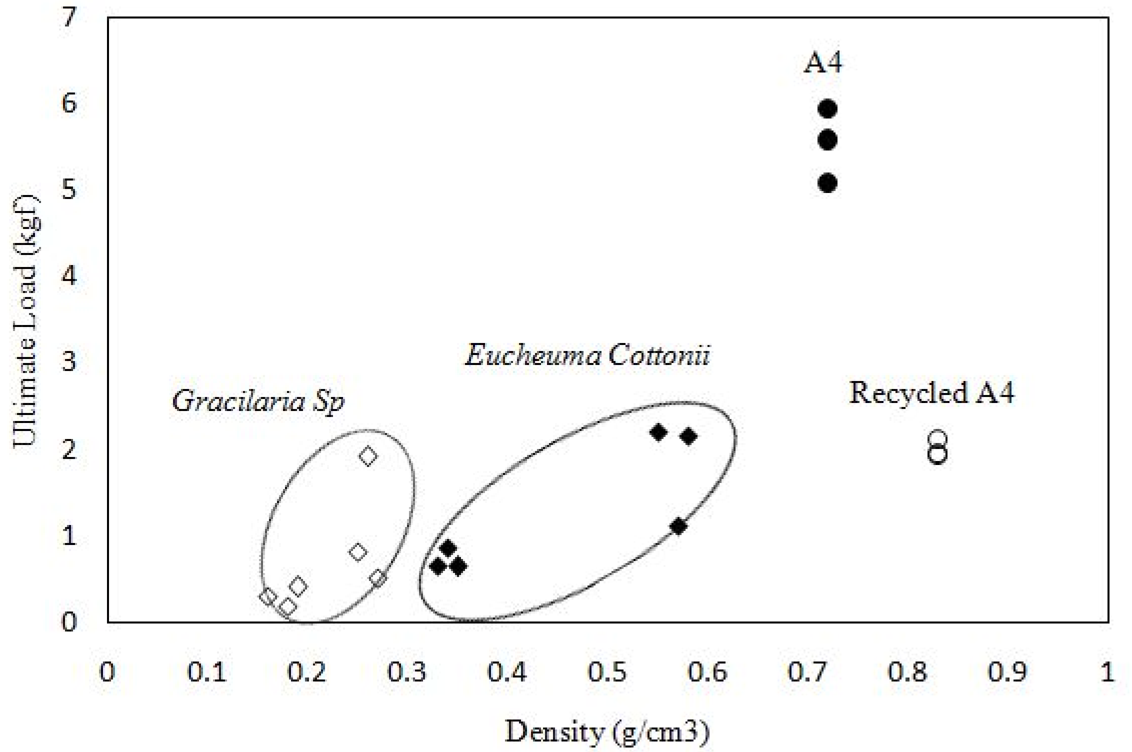

Figure 11. Density-based tensile ultimate load of algae paper without use of adhesive

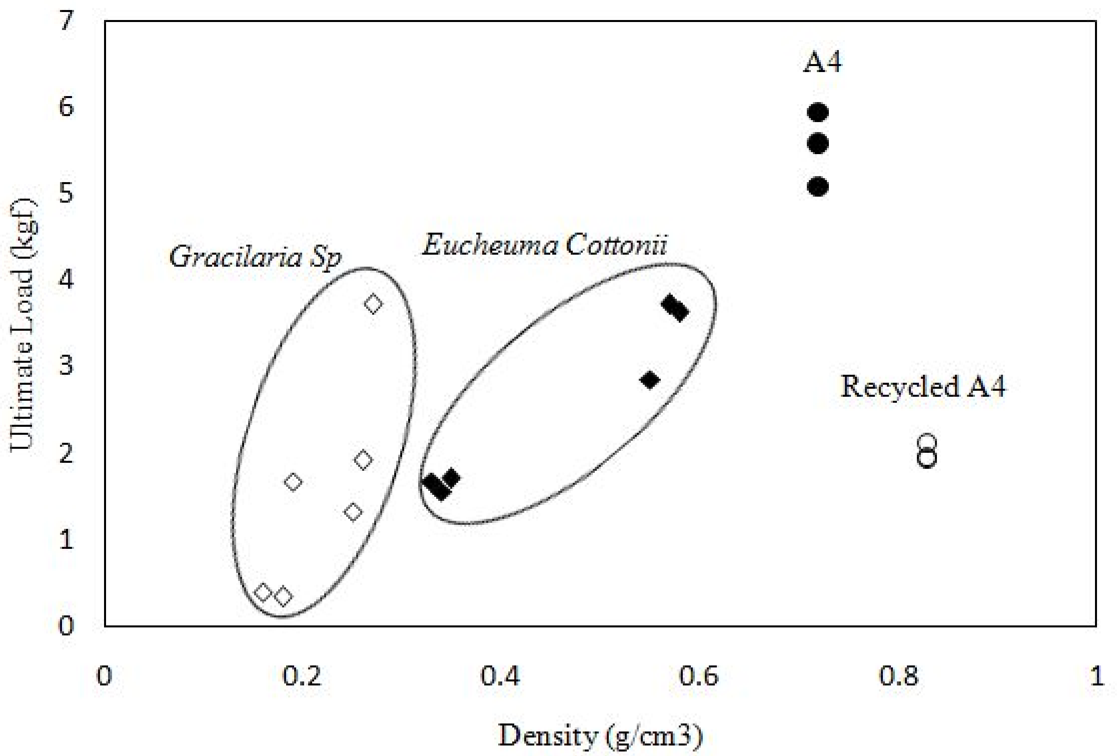

Figure 12. Density-based tensile ultimate load of algae paper with use of adhesive

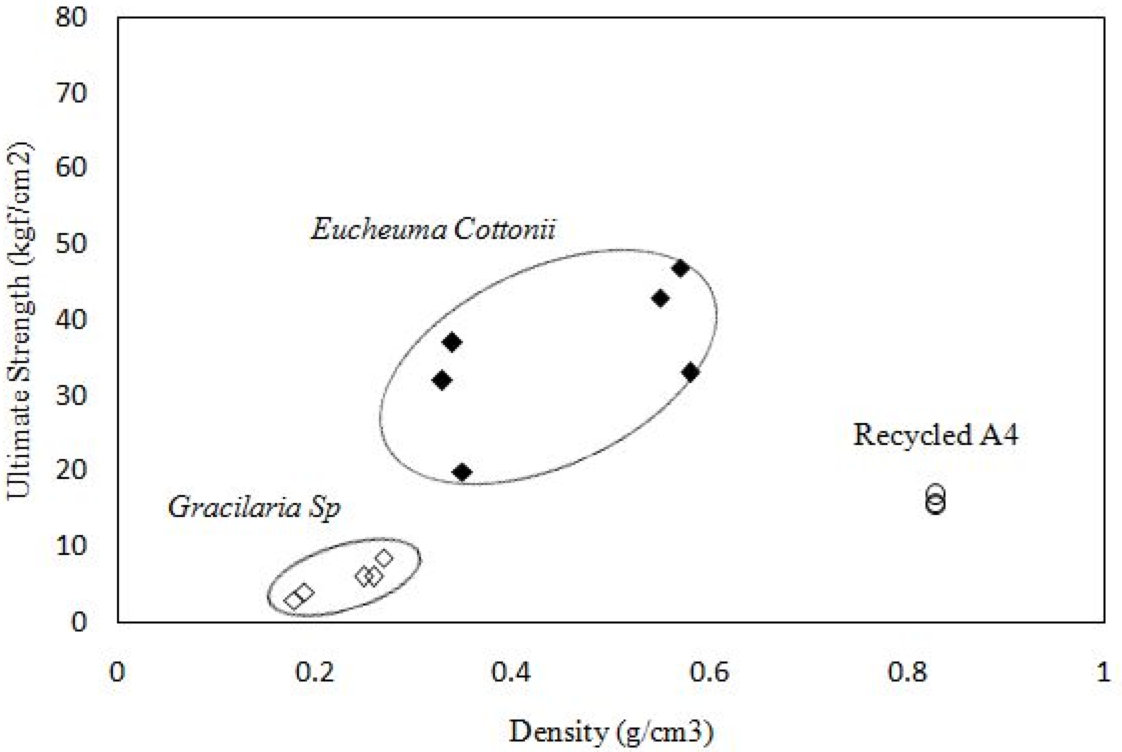

Figure 13. Density-based ultimate tensile strength of algae paper without use of adhesive

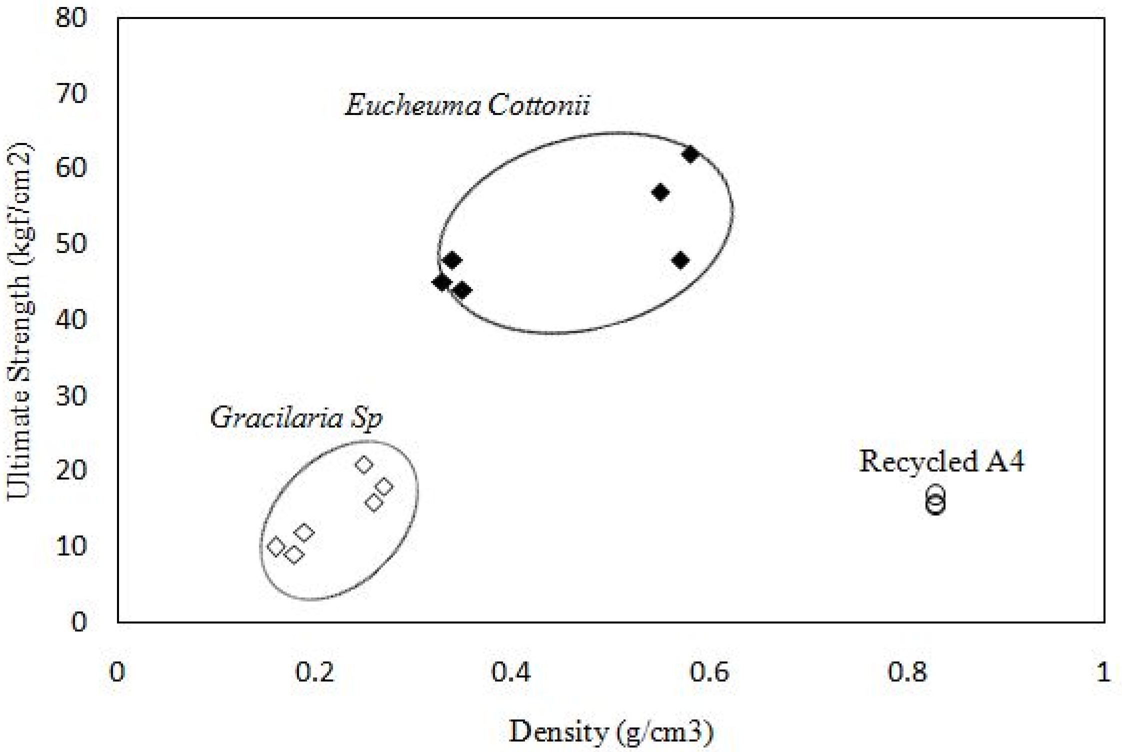

Figure 14. Density-based ultimate tensile strength of algae paper with use of adhesive

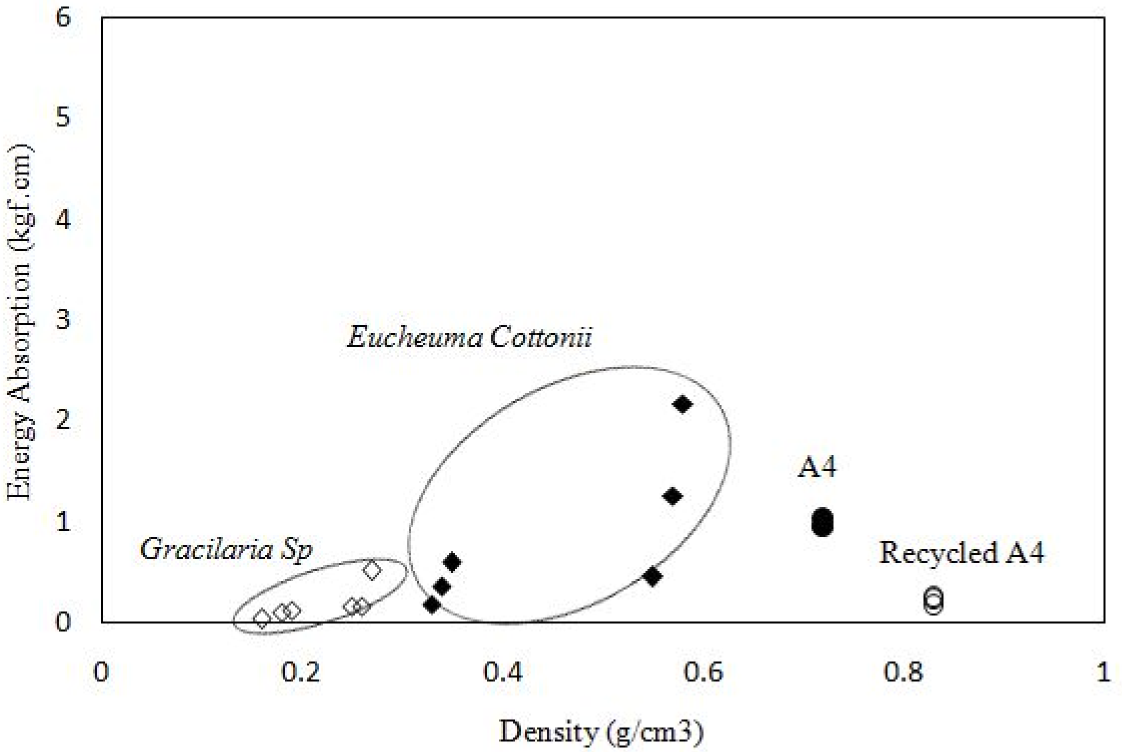

Figure 15. Density-based tensile energy absorption of algae paper without use of adhesive

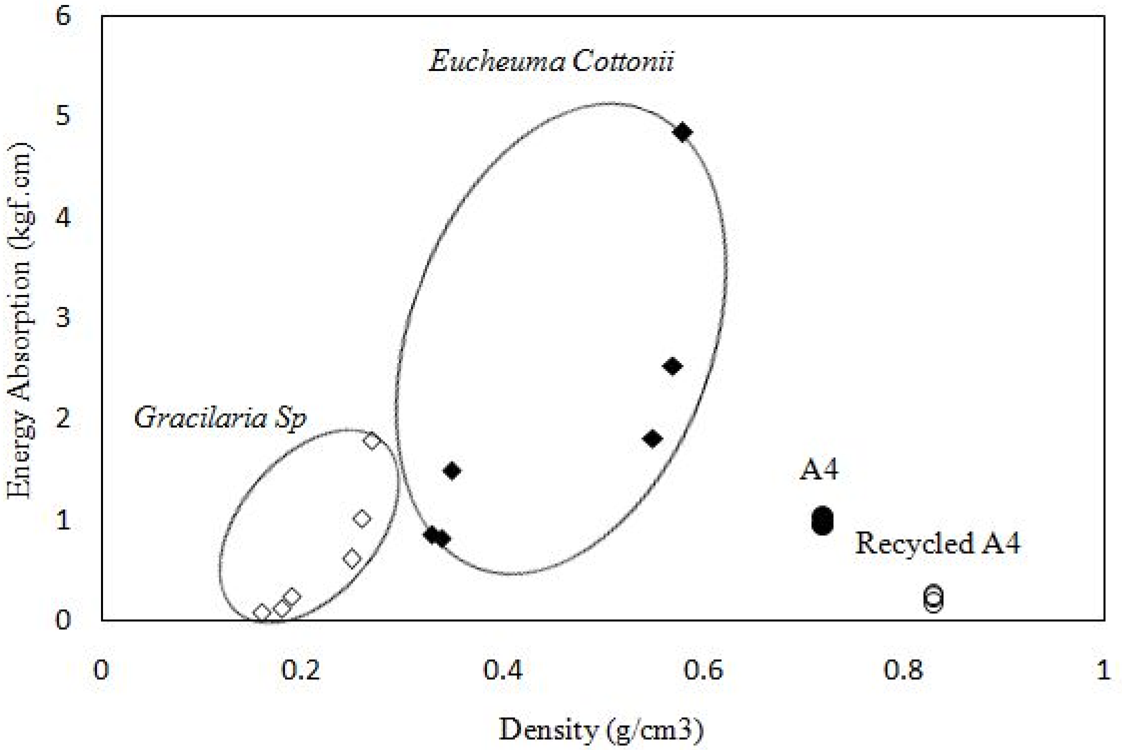

Figure 16. Density-based tensile energy absorption of algae paper with use of adhesive

Table 2. Tensile strength of the office copy paper (A4, 70 gsm)

Office copy paper	Bulk density (g/cm^3)	Ultimate tensile strength (kgf/cm^2)
A4-1	0.632	232.5
A4-2	0.635	271.8
A4-3	0.637	255.4

Conclusions

A work to mechanically study the potential use of the red algae pulps as raw material for papermaking has been conducted. Results obtained under the tensile testing showed that pulps made of the red algae would be the alternative to those of the wood and other natural fibers as raw materials for papermaking. With further improvement on the preparation method of the pulps and production method of paper as well, tensile properties of the paper made of the red algae will also be better improved.

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